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Patent Abstracts of Japan

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TITLE : ULTRAVIOLET-CURABLE COMPOSITION

ABSTRACT : PROBLEM TO BE SOLVED: To obtain a composition as an adhesive to be used in mutually laminating two disks on or both of which has an information-recorded layer, good in curability and causing no substrate deterioration, and affording highly reliable digital video disks in high productivity with short-time curing.

SOLUTION: This ultraviolet-curable composition contains, as photopolymerization initiator, at least each one kind of compound, namely: (A) compound highly sensitive to even ultraviolet light attenuated after transmitted through an information-recorded layer and the like and having a molar extinction coefficient of ≥ 50 (l/mol cm) in the wavelength band of 370 to 450nm and (B) different compound hardly subject to oxygen inhibition and of intramolecular cleavage type or hydrogen pull-off type.

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(54) [Title of the Invention]

Ultraviolet Curable Type Composition

(57) [Abstract]

[Objective] To present an ultraviolet curable type composition as the adhesive which is used for mutually laminating two discs wherein at least one disc has an information recorded layer, it has excellent curability without causing substrate deterioration and highly reliable digital disc with high productivity in short time curing is obtained.

[Solution] The ultraviolet curable type composition which is characterized by respectively comprising at least more than one kind of compounds as the photopolymerization initiators which compound sensitively react to even attenuated ultraviolet rays transmitted through the information recorded layer, etc., and hardly affect oxygen inhibition, that is to say, photopolymerization initiator (A) which has the point that the molar decadic absorption coefficient is more than 50 (l/mol cm) in the wave range from 370nm to 450nm, and photopolymerization initiator (B) which is an intramolecular cleavage type or a hydrogen abstraction type and does not belong to (A).

[Claims]

[Claim 1] The ultraviolet curable type composition which is characterized by respectively comprising at least more than one kind of photopolymerization initiator selected from the photopolymerization initiator groups (A) and (B) as the adhesive which is used for mutually laminating two discs wherein at least one disc has an information recorded layer.

(A) the photopolymerization initiator which has the point that the molar decadic absorption coefficient is more than 50 (l/mol cm) in the wave range from 370nm to 450nm.

(B) the photopolymerization initiator which is an intramolecular cleavage type or a hydrogen abstraction type and does not belong to (A).

[Claim 2] The ultraviolet curable type composition described in Claim 1 which is characterized by using the photopolymerization initiator which has the point that the molar decadic absorption coefficient is more than 500 (l/mol cm) in the wave range from 370nm to 450nm as foresaid photopolymerization initiator (A).

[Claim 3] The ultraviolet curable type composition which is characterized by using 0.1 ~ 10 parts by weight of the photopolymerization initiator described in Claim 1 or Claim 2.

[Claim 4] The ultraviolet curable type composition described in Claim 1, 2 or 3 which is used for mutually laminating two discs in which the disc having an information recorded layer and the disc which does not have an information recorded layer are polycarbonate substrates.

[Claim 5] The adhesive is the ultraviolet curable type composition described in Claim 1, 2, 3 or 4 which comprises more than two kinds of multifunctional (meth) acrylate having more than two (meth) acryloyl groups as the essential component.

[Detailed Description of the Invention]

[0001] The present invention relates to the adhesive which is used at the time for mutually laminating two discs wherein at least one disc has an information recorded layer, in further detail, the present invention relates to the ultraviolet curable type composition which is used as the adhesive.

[0002] [Prior Art]

Digital video disc (DVD) which is a high density information recorded medium is prepared by the method of mutually laminating two discs in which at least one disc has an information recorded layer, and usage of an ultraviolet curable type composition as the adhesive has been actively studied.

[0003] In the case of rewritable type DVD, as the two discs laminated, there is the case of using heat resistance thermoplastic resin substrates represented by polycarbonate wherein unevenness which corresponds to the recorded information is provided on one surface, and aluminum, metal, etc., layer is furthermore formed as a thin metal film, or there is the case of using transparent heat resistance thermoplastic resin substrates wherein one substrate does not have an information recorded layer, etc., the substrate is appropriately selected according to the purpose.

[0004] First, the two discs are required to securely adhere in ordinary condition, and no deformation and no appearance variation of the laminated discs are required of course in the ordinary condition and after environmental test under high temperature and high humidity.

The characteristics of using an adhesive highly affects the change of the laminated discs after environmental tests, and some kinds of adhesive allow the development of pinholes in the metal thin film layer provided as the information recorded layer, or deteriorate the transparent heat resistance thermoplastic resin substrate to whitish.

[0005] Ultraviolet curable type composition used which highly influence deterioration of the substrate, etc., like these have been well known, generally it has been thought that the influence of monomer and oligomer is high.

[0006] However, deterioration of the substrate, etc., is not concluded only for that reason; even when a reactive component from which relatively less deterioration of the substrate, information recorded layer, etc., is expected is selected, that these are highly affected by the kind of photopolymerization initiator included in the ultraviolet curable composition has been known in the knowledge of the present inventors.

[0007] [Problems Solved by the Invention]

The present invention was done in consideration of conditions like this, and the objective of the present invention is to present an ultraviolet curable type composition which offers a curable substance which does not develop deterioration of the substrate and information recorded layer under severe environment.

[0008] [Method for Solving the Problems]

The present inventors have studied hard to solve the problems described above, and it resulted in the deterioration degree of the substrate and information recorded layer are quite different under severe environment even in the case of identical reactive monomer and oligomer components and only the component of the photopolymerization initiator is varied, and in the case of using an ultraviolet curable type composition as the adhesive for DVD, it was found that selection of the photopolymerization initiator is extremely important from the viewpoint of not only curability but also substrate deterioration and the present invention was accomplished.

[0009] That is to say, the present invention is to present an ultraviolet curable type composition which is characterized by respectively comprising at least more than one kind of photopolymerization initiators selected from the photopolymerization initiator groups (A) and (B) described below as the adhesive which is used for mutually laminating two discs wherein at least one disc has an information recorded layer.

(A) the photopolymerization initiator having the point that the molar decadic absorption coefficient is more than 50 (l/mol cm) in the wave range of 370nm to 450nm.

(B) the photopolymerization initiator which is an intramolecular cleavage type or a hydrogen abstraction type and does not belong to (A).

[0010] In the photopolymerization initiators which use in the present invention, as the photopolymerization initiators belonging to (A), there are, for example, benzoin isobutyl ether, 2,4-diethyl thioxanthone, 2-isopropyl thioxanthone, 2-chlorothioxanthone, benzyl, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, bis (2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide, etc. These (A) groups are to sensitively react to even extremely attenuated weak ultraviolet rays.

[0011] In these photopolymerization initiators, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, bis (2,6-dimethoxybenzoyl)-2,4,4-

trimethyl pentyl phosphine oxide, etc., are to sensitively react to the ultraviolet rays transmitted through the substrate, therefore curability is excellent, on the other hand, in the case of using this independently, there is the tendency to cure insufficiently at the part that touches air, because this easily affects oxygen inhibition.

[0012] As the photopolymerization initiator, the photopolymerization initiator which has the point that the molar decadic absorption coefficient is more than 50 (l/mol cm), especially preferably more than 500 (l/mol cm) in the wave range from 370nm to 450nm is better.

[0013] The photopolymerization initiator belonging to (B) can be used in combination to dissolve this disadvantage, as the intramolecular cleavage type, benzoyl ethyl ether, benzyldimethyl ketal, 1-hydroxycyclohexyl phenylketone, 2-hydroxy-2-methyl-1-phenyl-propane-1-on, 1-(4-isopropyl phenyl)-2-hydroxy-2-methylpropane-1-on, 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propanone-1-on, etc., can be listed.

[0014] Furthermore, as the hydrogen abstraction type, for example, 4-phenylbenzophenone, isophthalophenone, 4-benzoyl-4'-methyl-diphenyl sulfide, etc., can be listed. These (B) groups are difficult to affect the polymerization inhibition by oxygen.

[0015] The combined proportion of the photopolymerization initiator groups (A) and (B) is not especially limited, however, usually (A) group/(B) group (weight ratio) = 20/80 ~ 80/20, preferably 60/40 ~ 40/60.

[0016] Furthermore, as the photosensitizer, for instance, amines which do not cause addition polymerization reaction with the polymerizable component described later, for example, triethylamine, methyldiethanolamine, triethanolamine, diethylaminoacetophenone, p-diethylaminoacetophenone, p-dimethylaminoethyl benzoate, p-dimethylamino isoamyl benzoate, N,N-dimethyl benzylamine, 4,4'-bis (diethylamino) benzophenone, etc., can also be used in combination with the photopolymerization initiator described above.

Of course, photopolymerization initiator and photosensitizer having excellent solubility in the curable component, and which do not inhibit the ultraviolet ray transmittability may be preferably used.

[0017] At the time of preparing the ultraviolet curable composition, monofunctional (meth) acrylate and polyfunctional (meth) acrylate can be used as the polymerizable monomer components. These are

respectively, independently or more than two kinds of these can be used in combination. However, the compositions may preferably be prepared by using more than two kinds of polyfunctional (meth) acrylate having more than two (meth) acryloyl groups.

[0018] As the polymerizable monomers which can be used in this invention, for example, there are as follows. As the monofunctional (meth) acrylate, for example, there are (meth) acrylate, etc., having a group as the substituent such as methyl, ethyl, propyl, butyl, amyl, 2-ethylhexyl, octyl, nonyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, benzyl, methoxyethyl, butoxyethyl, phenoxyethyl, nonyl phenoxyethyl, tetrahydrofurfuryl, glycidyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-chloro-2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl, nonyl phenoxyethyl tetrahydrofurfuryl, caprolactone denatured tetrahydrofurfuryl, isobornyl, dicyclopentanyl dicyclopentenyl, dicyclopentenyl oxyethyl (_ is phonetic), etc., can be listed.

[0019] Furthermore, as the polyfunctional (meth) acrylate, for example, diacrylate such as 1,3-butylene glycol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,8-octanediol, 1,9-nonanediol, tricyclodecane dimethanol, ethylene glycol, polyethylene glycol, propylene glycol, tripropylene glycol, etc.; di(meth) acrylate such as tris (2-hydroxyethyl) isocyanurate; diol di (meth) acrylate obtained by adding more than 4 mol ethylene oxide or propylene oxide to 1 mol neopentyl glycol; diol di (meth) acrylate obtained by adding 2 mol ethylene oxide or propylene oxide to 1 mol bisphenol A; triol di or tri (meth) acrylate obtained by adding more than 3 mol ethylene oxide or propylene oxide to 1 mol trimethylol propane; diol di (meth) acrylate obtained by adding more than 4 mol ethylene oxide or propylene oxide to 1 mol bisphenol A; tris (2-hydroxyethyl) isocyanurate tri (meth) acrylate; trimethylol propane tri (meth) acrylate; pentaerythritol tri (meth) acrylate; dipentaerythritol poly (meth) acrylate; caprolactone denatured tris [(meth) acryloxy ethyl] isocyanurate; alkyl denatured dipentaerythritol poly (meth) acrylate; caprolactone denatured dipentaerythritol poly (meth) acrylate; hydroxy pivalic acid neopentyl glycol diacrylate; caprolactone denatured hydroxy pivalic acid neopentyl glycol diacrylate; ethylene oxide denatured phosphoric acid (meth) acrylate; ethylene oxide denatured alkylated phosphoric acid (meth) acrylate, etc., are listed.

[0020] Furthermore, N-vinyl-2-pyrrolidone, acryloyl morpholine, vinyl imidazole, N-vinyl caprolactam, vinyl acetate, methacrylic acid, methacrylamide, N-hydroxymethylacrylamide or N-hydroxyethyl acrylamide and their alkyl ether compound can also be used.

[0021] Furthermore, as the polymerizable oligomers which can be used in combination similarly to the polymerizable monomers, there are polyester acrylate, polyether acrylate, epoxy acrylate, urethane acrylate, etc.

[0022] To obtain higher adherence to the information recorded layer which main body is a metal thin film, (meth) acrylate compound having a functional group comprised of phosphoric acid or its derivative can be included in the composition, for further improvement of hardness, (meth) acrylate compound having larger number of (meth) acryloyl group in one molecule can be included, and to adjust the elastic modulus, etc., relatively high molecular polymeric component such as polymerizable oligomer can be included.

[0023] As the ultraviolet curable type composition, the liquid state at ordinary temperature to 40°C is preferably used. Solvent is preferably not used, even if it is used, an extremely small amount is preferable.

Furthermore, in the case of coating aforesaid composition by the spin coater, the viscosity is preferably adjusted to 20 ~ 1000 centipoise, and in the case of relatively thick film, the viscosity is preferably adjusted to 100 ~ 1000 centipoise.

[0024] In this invention, said information recorded layers side are mutually adhered, however exposed information recorded layers may be directly adhered, the protective coated layers which protect the exposed surfaces of the information recorded layers, and these protective coated layers may be mutually adhered. In this case, these protective coated layers are usually formed with a curable substance of the ultraviolet curable type composition. In that case, this protective coated layer needs to be transmittable to the ultraviolet rays.

The ultraviolet curable type composition for the protective coated layer is preferably prepared to have excellent adherence to both the exposed surface of the information recorded layer and the cured substance of the ultraviolet curable type composition to mutually adhere the discs.

[0025] Furthermore, to the composition in the present invention, if necessary, furthermore other additives such as thermal polymerization inhibitor, antioxidant represented by hindered phenol, hindered amine, phosphite, etc., plasticizer, silane coupling agent represented by epoxy silane, mercapto silane, (meth) acryl silane, etc., can also be blended for the purpose of improving various kinds of characteristics. Those

having excellent solubility in the curable component and which do not inhibit the ultraviolet ray transmittability are selected and used.

[0026] In the case of preparing the composition in the present invention, not only the photopolymerization initiator described above, chemical compositions such as the physical properties of the composition itself and the physical properties of the laminated cured layers are appropriately selected to be suitable for DVD.

[0027] No deterioration of the information recorded to the information recorded layer, that is to say, without the occurrence of abnormality to the pitch is a prerequisite for the criterion for selecting the chemical compositions, for example, the component in the composition does not crystallize and does not occur phase separation, it has as high as possible wettability even for two surfaces laminated it has leveling which gives a smooth and uniform wet surface in a short time, it does not include substance and ion which cause corrosion and deterioration of the two surfaces laminated, the composition before curing and even in the liquid state has some extent of adherence, it has as low as possible gas solubility which causes hardening inhibition, the composition has transparency before curing and after curing for transmitting the ultraviolet rays at as high a ratio as possible, the refractive index and hardness of the adhesive layer after curing and the heat resistance thermoplastic resin which constructs the substrate are as similar as possible, to make higher adherence of the two layers laminated and the cured layer, the elastic modulus of the same cured layer is set in a specific range, the water vapor permeability is set as low as possible, the shrinkage factor of said composition before curing and after curing is set as low as possible, and the measured value of these respective evaluation items are excellent as the absolute value, and also variation between these respective absolute values are as low as possible when it is exposed in ordinary condition and at high temperature and humidity for a long time, etc., are listed. The ultraviolet curable type composition which comprises photopolymerization initiator is prepared so as to completely satisfy these criterions or to satisfy as many as possible.

[0028] Furthermore, as the ultraviolet ray irradiation system for curing the composition in the present invention, other than using continuous ultraviolet ray irradiation which is generally widely done, the flash irradiation system which irradiates a similar quantity or less quantity of rays as the irradiation quantity of rays which is required for curing by conventional continuous ray irradiation, for example, $\mu\text{sec} \sim \text{msec}$ order at once in a short time may be used.

[0029] Irradiation of rays may be done only from one side surface of the discs mutually facing each other, however it can also be done from both surfaces.

[0030] The composition by the present invention is, in the manufacturing method for digital video disc, for example, especially effective for adhering one disc substrate wherein the information recorded thin film is laminated to the heat resistance thermoplastic resin and the substrate comprised of only heat resistance thermoplastic resin.

The prevention effectiveness of the opaqueness and whitish of the substrate under severe environmental conditions is significant in the case of constructing that of heat resistance thermoplastic resin is polycarbonate.

[0031] In this case, each substrate mutually faces each other, thereafter, usually, these are adhered by curing the composition by the present invention by irradiating ultraviolet rays from the substrate side comprised of only heat resistance thermoplastic resin.

[0032] [Embodiment of the Present Invention]

Following, the embodiment in the present invention will be explained on the basis of the preferable state.

First, one disc shaped plastic substrate wherein a metal thin film of 400 ~ 600 angstroms is laminated, and one substrate comprised of only disc shaped plastic are prepared.

[0033] First, a composition is prepared by using more than two kinds of polyfunctional (meth) acrylate having more than two (meth) acryloyl groups are the essential and principal components, and using polymerizable monomer if necessary, and using a total of 2 ~ 7 parts by weight of photopolymerization initiator (A) having an absorption wavelength in the range of more than 370nm, and having the point that the molar decadic absorption coefficient is more than 50 (l/mol cm) in the wave range from 370nm to 450nm, and the photopolymerization initiator (B) which is an intramolecular cleavage type or a hydrogen abstraction type and does not belong to (A) per 100 parts by weight of the liquid state ultraviolet curable type composition. But, benzophenone is not included in this composition.

[0034] More preferable selective combination of photopolymerization initiators (A) and (B) are as described below.

The photopolymerization initiator group (A): which has the point that the molar decadic absorption coefficient is more than 500 (l/mol cm) in the wave range from 370nm to 450nm.

The photopolymerization initiator group (B): benzoyl ethyl ether, benzyldimethyl ketal, 1-hydroxycyclohexyl phenylketone, 2-hydroxy-2-methyl-1-phenyl-propane-1-on, 1-(4-isopropyl phenyl)-2-hydroxy-2-methylmethylpropane-1-on, and 2-methyl-1-(4-methylthiophenyl)-2-morpholino-propanone-1-on (above are intramolecular cleavage type photopolymerization initiators), 4-phenylbenzophenone, isophthalophenone, 4-benzol-4'-methyl-diphenyl sulfide (above are hydrogen abstraction type photopolymerization initiators).

[0035] Aforesaid composition was coated on the surface of the metal thin film of aforesaid substrate, both surfaces of the substrate were laminated, and both substrates were adhered by irradiating ultraviolet rays from both surfaces of the plastic substrates, and was a DVD.

[0036] [Examples]

Following, the present invention will be explained in detail according to the examples, however the present invention is not limited by these examples. Furthermore, "part" in the examples is expressed "parts by weight".

[0037] [Example 1]

20 parts by weight of neopentyl glycol diacrylate, 20 parts by weight of diacrylate of diol in which 2 mol ethylene dioxide was reacted with one mol bisphenol A, 30 parts by weight of trimethylol propane triacrylate, 26 parts by weight of urethane acrylate which was obtained by reacting 1 mol polytetramethylene glycol (molecular weight of 850) with 2 mol tolylene diisocyanate and thereafter reacting with 2 mol hydroxyethyl acrylate, as the photopolymerization initiators, 2 parts by weight of 2,4,6-trimethylbenzoyl diphenylphosphine oxide, and 2 parts by weight of benzyldimethyl ketal were mixed and melted at a temperature of 60°C for one hour, and an ultraviolet curable type composition which was a pale yellow color and transparent was prepared.

A laminated disc was prepared by using this composition and by the test method 1 described below, and the tackiness was tested by touching the end surface of the disc with finger, and there was no tackiness.

Furthermore, this disc was placed under an environment at a temperature of 85°C and 95% RH for 96 hours and the external appearance was observed, it resulted in there was absolutely no change compared to that before the environmental test.

[0038] [Test Method 1]

Two disc shaped polycarbonate substrates having a diameter of 12cm wherein aluminum which film thickness was 500 angstroms were formed as the metal thin films were prepared, the composition described above was coated to one of those disc shaped polycarbonate substrates with a dispenser, and thereafter the other substrate was superposed on it.

The coating amount of the composition described above was so that the thickness of the film of said composition at the time of spreading it only the weight of the substrate was set to become 20 ~ 50µm. Thereafter, it was cured by using a belt conveyer system ultraviolet ray irradiation device equipped with a convergent type metal halide lamp which irradiation intensity was adjusted to 55 mW/cm² (cold mirror was attached, lamp output was 80 W/cm), and the conveyer speed was 3 m/min (irradiation quantity of rays was approximately 230 mJ/cm²). Furthermore, ray irradiation was done from both surfaces of the two polycarbonate substrates.

[0039] [Example 2]

The polymerizable components were the same as in Example 1 described above, and as the photopolymerization initiators, 2 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-butanone-1- and 2 parts by weight of benzyldimethyl ketal were mixed and melted at a temperature of 60°C for one hour and an ultraviolet curable type composition which was a pale yellow color and transparent was prepared.

A laminated disc was prepared by using this composition and in a similar manner as Example 1, and the tackiness was tested by touching the end surfaces of the disc with finger, there was no tackiness.

The disc was placed under an environment of a temperature of 85°C and 95% RH for 96 hours and the external appearance was observed, it resulted in there was absolutely no change compared to that before the environmental test.

[0040] [Example 3]

The polymerizable components were the same as Example 1 described above, and as the photopolymerization initiators, 2 parts by weight of 2,4,6-trimethylbenzoyl diphenylphosphine oxide, and

2 parts by weight of benzyldimethyl ketal were mixed and melted at a temperature of 60°C for one hour, and an ultraviolet curable type composition which was a pale yellow color and transparent was prepared.

A laminated disc was prepared by using this composition and by the test method 2 described below, and the tackiness was tested by touching the end surface of the disc with finger, and there was no tackiness.

The disc was placed under an environment of a temperature of 85°C and 95% RH for 96 hours, and it resulted in there was absolutely no change compared with that before the environmental test.

[Test Method 2]

The composition described above was coated on the disc shaped polycarbonate substrate having a diameter of 12cm wherein aluminum thin film thickness of 500 angstroms was formed as the metal thin film by a dispenser, thereafter a transparent disc shaped polycarbonate substrate having a diameter of 12cm was superposed.

The coating amount of the composition described above was so that the thickness of the film of said composition at the time of spreading it only the weight of the substrate was set to become 20 ~ 50μm.

Thereafter, it was cured by using this belt conveyer system ultraviolet ray irradiation device equipped with a convergent type metal halide lamp which irradiation intensity was adjusted to 55mW/cm² (cold mirror was attached, lamp output was 80 W/cm), and a conveyer speed to 3 m/min (irradiation quantity of rays was approximately 230 mJ/cm²).

Furthermore, ray irradiation was done from both surfaces of the polycarbonate substrate comprised of only polycarbonate and the polycarbonate substrate wherein aluminum thin film was laminated.

[0041] [Example 4]

The polymerizable components were the same as Example 1 described above, and as the photopolymerization initiators, 2 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholino phenyl)-1-butanone-1, and 2 parts by weight of benzyldimethyl ketal were mixed and melted at a temperature of 60°C for one hour, and an ultraviolet curable type composition which was a pale yellow color and transparent was prepared.

A laminated disc was prepared by using this composition and in a similar manner as Example 3, and the tackiness was tested by touching the end surface of the disc with finger, there was no tackiness.

Furthermore, this disc was placed under an environment of a temperature of 85°C and 95% RH for 96 hours, and it resulted in there was absolutely no change compared with that before the environmental test.

[0042] Either photopolymerization initiators in the (A) group in Examples 1 ~ 4 have an absorption wavelength in the range of more than 370nm, and have the point that the molar decadic absorption coefficient is more than 500 (l/mol cm) in the wave range from 370nm to 450nm.

[0043] Furthermore, a DVD in which the metal thin film layers sides of the heat resistance thermoplastic resin substrates are mutually laminated by using the compositions in Examples 1 ~ 4, and a DVD in which the metal thin film layer side of the heat resistance thermoplastic resin substrate and the substrate comprised of only heat resistance thermoplastic resin are laminated by using the compositions in Examples 1 ~ 4, in either case, deterioration of the DVD is not seen for example, even under severe environment of high temperature and high humidity for a long time.

[0044] Furthermore, the compositions in Examples 1 ~ 4 also have the following two advantages other than the technical advantage described above. That is to say, the compositions in Examples 1 ~ 4 have excellent curability in that curing and bonding can be efficiently done, and have the excellent point that tackiness is not recognized even at the part from the end surface of the laminated disc.

[0045] Either of the compositions in Examples 1 ~ 4 are preferable as the ultraviolet curable type composition which is used as the adhesive for laminating system of DVD.

[0046] Furthermore, in the examples, continuous lighting light which is generally widely done is used as the ultraviolet light irradiation system, however the flash system irradiation system as described above may of course be used.

[0047] [Effectiveness of the Invention]

By using the composition in the present invention, deterioration of the laminated disc does not occur even after exposure to severe environment in the environmental test at high temperature and high humidity, therefore a DVD having high durability and reliability can be produced.

Translator's Note: there are molar decadic absorption coefficient which say 50 (l/mol cm) and some which say 500 (l/mol cm)

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(57) 【要約】

【課題】 少なくとも 1 枚のディスクに情報記録層を有する 2 枚のディスクを貼り合わせる際に使用する接着剤として、硬化性に優れかつ基板の変質を起こさない、短時間硬化で生産性に優れ、信頼性の高いデジタルビデオディスクが得られる紫外線硬化型組成物を提供する。

【解決手段】 光重合開始剤として、情報記録層等を透過し減衰した紫外線にも鋭敏に反応するものと、酸素阻害を受けにくいもの、即ち (A) 波長領域 370 nm から 450 nm において、モル吸光係数が 50 (l/mol*cm) 以上となる点を有するものと、(B) 分子内開裂型または水素引き抜き型で (A) に属さないものを各々 1 種以上含むことを特徴とする紫外線硬化型組成物。

【特許請求の範囲】

【請求項 1】 少なくとも 1 枚のディスクに情報記録層を有する 2 枚のディスクを貼り合わせる際に使用する接着剤として、下記光重合開始剤群 (A) 及び (B) から選択された各々 1 種類以上含むことを特徴とする紫外線硬化型組成物。

(A) 波長領域 370 nm から 450 nm において、モル吸光係数が 50 (l/mol*cm) 以上となる点を有する光重合開始剤。

(B) 分子内開裂型または水素引き抜き型で (A) に属さない光重合開始剤。

【請求項 2】 前記光重合開始剤群 (A) として、波長領域 370 nm から 450 nm において、モル吸光係数が 500 (l/mol*cm) 以上となる点を有するものを用いることを特徴とする請求項 1 記載の紫外線硬化型組成物。

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(57) [Abstract]

[Problem] At least, property change of being superior and substrate is not caused in curability as adhesive which is used occasionally where 2 disk which possesses information recording layer in disk of one layer is pasted together, in rapid curing it is superior in productivity, it offers the ultraviolet light-curable composition where digital video disk where reliability is high is acquired.

[Means of Solution] As photoinitiator, those which are difficult to receive thing and the oxygen inhibition which acutely react to also ultraviolet light which transmits information recording layer and etc attenuation it does. Namely ultraviolet light-curable composition which designates that each one kind or more it includes those which do not belong to (A) with thing and (B) intramolecular cleavage type or the hydrogen-abstracting type which possess point where molar absorptivity becomes 50 (l/mol*cm) or greater from the (A) wavelength region 370 nm in 450 nm, as feature.

[Claim(s)]

[Claim 1] At least each 1 kind or more which is selected from the below-mentioned photoinitiator group (A) and (B) as adhesive which is used occasionally where 2 disk which possesses information recording layer in disk of one layer is pasted together, ultraviolet light-curable composition which designates that it includes as feature.

(A) From wavelength region 370 nm in 450 nm, photoinitiator which possesses point where the molar absorptivity becomes 50 (l/mol*cm) or greater.

(B) Photoinitiator which does not belong to (A) with intramolecular cleavage type or the hydrogen-abstracting type.

[Claim 2] Aforementioned photoinitiator group (A) as, from wavelength region 370 nm in 450 nm, the ultraviolet light-curable composition which is stated in Claim 1 which designates that those which possess point where molar absorptivity becomes 500 (l/mol*cm) or greater are used as feature.

【請求項 3】請求項 1 または 2 記載の光重合開始剤を 0.1 ～ 10 部使用したことを特徴とする紫外線硬化型組成物。

【請求項 4】貼り合わせる 2 枚のディスクが、情報記録層を有するディスクと情報記録層を有しない透明なポリカーボネート基板である、請求項 1、2 または 3 記載の紫外線硬化型組成物。

【請求項 5】接着剤が、2 以上の（メタ）アクリロイル基を有する多官能（メタ）アクリレート of the 2 種以上を必須成分として含む紫外線硬化型組成物である請求項 1、2、3 または 4 記載の組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、少なくとも 1 枚のディスクに情報記録層を有する 2 枚のディスクを貼り合わせる際に使用する接着剤に関し、更に詳しくは接着剤として使用する紫外線硬化型組成物に関する。

【0002】

【従来の技術】高密度情報記録媒体であるデジタルビデオディスク（DVD）は、少なくとも 1 枚のディスクに情報記録層を有する 2 枚のディスクを貼り合わせる方法で作製され、紫外線硬化型組成物を接着剤として使用することが盛んに検討されている。

【0003】再生専用型の DVD の場合、貼り合わせる 2 枚のディスクとして、共にポリカーボネートに代表される耐熱性熱可塑性樹脂基板の片面に記録情報に対応する凹凸を設け、更に金属薄膜として例えばアルミニウムや金等の層が形成されているものを使用したり、1 枚には情報記録層を持たない透明な耐熱性熱可塑性樹脂基板を使用する場合等があり、用途に応じ適宜基板が選択される。

【0004】まず、2 枚のディスクは常態で確実に接着されることが必要で、しかも貼り合わせられたディスクは、常態においては勿論のこと、高温高湿の環境試験後においても変形がなく外観上の変化もないことが求められている。環境試験後の変化に対しては、使用する接着剤の特性が大きく影響し、接着剤の種類によっては情報記録層として設けられている金属薄膜層にピンホールを発生させたり、透明な耐熱性熱可塑性樹脂基板を白っぽ

[Claim 3] Ultraviolet light-curable composition which designates that 0.1 to 10 part you use photoinitiator which is stated in Claim 1 or 2 as feature.

[Claim 4] 2 disk which it pastes together, it is a transparent polycarbonate substrate which it does not possess disk and information recording layer which possess information recording layer, ultraviolet light-curable composition which is stated in Claim 1, 2 or 3.

[Claim 5] Adhesive, composition which is stated in Claim 1, 2, 3 or 4 which is a ultraviolet light-curable composition which includes 2 kinds or more of polyfunctional (meth)acrylate which possesses (meth) acryloyl group of the 2 or more as essential component.

[Description of the Invention]

[0001]

[Technological Field of Invention] This invention regards adhesive which is used occasion where 2 disc which at least possesses information recording layer in disc of one layer is pasted together, furthermore details regard ultraviolet light-curable composition which you use as the adhesive.

[0002]

[Prior Art] Digital video disk (DVD) which is a high density information storage medium is produced with method which pastes together 2 disk which at least possesses information recording layer in disk of the one layer, using ultraviolet light-curable composition as adhesive is examined actively.

[0003] When of DVD of read-only type, relief which corresponds to recorded information in one surface of heat resistant thermoplastic resin substrate which is represented together in polycarbonate as 2 disk which it pastes together, is provided, those where for example aluminum and gold or other layer are formed furthermore as metal thin film are not used, when transparent heat resistant thermoplastic resin substrate which the information recording layer does not have is used in one layer etc, it is, as needed substrate is selected according to application.

[0004] First, as for 2 disk being necessary to glue securely with the ordinary state, furthermore disk which is pasted together regarding the ordinary state of course, without being deformation in after environmental test of the high temperature high humidity and being either change on external appearance is sought. Vis-a-vis change after environmental test, depending upon types of the adhesive it generates pinhole in metal thin film layer which characteristic of adhesive which is

く変質させることがある。

【0005】このような基板等の変質に関して、使用する紫外線硬化型組成物の影響が大きいことは既に良く知られており、一般的には、使用する反応性モノマーやオリゴマーの影響が大きいものと考えられていた。

【0006】しかしながら、基板等の変質は、それだけに帰結されるものではなく、比較的基板や情報記録層等の変質が少ないと予想される反応成分を選択しても、紫外線硬化性組成物に含まれる光重合開始剤の種類によっても、大きな影響を受けることが本発明者らの知見からもわかってきた。

【0007】

【発明が解決しようとする課題】本発明はかかる状況に鑑みてなされたものであり、厳しい環境下においても基板や情報記録層の変質を起こさない硬化物を与える紫外線硬化型組成物を提供することにある。

【0008】

【課題を解決するための手段】本発明者らは、上記課題を解決するために鋭意検討した結果、反応性モノマーやオリゴマー成分を同一にし、光重合開始剤成分のみを変えた場合でも、厳しい環境下においては基板や情報記録層の変質度合いが大きく異なり、DVD用の接着剤として紫外線硬化型組成物を使用する場合は、硬化性のみならず基板変質の観点からも光重合開始剤の選択は極めて重要であることを見出し本発明に至った。

【0009】すなわち本発明は、少なくとも1枚のディスクに情報記録層を有する2枚のディスクを貼り合わせ際に使用する接着剤として、下記光重合開始剤群(A)及び(B)から選択された各々1種類以上含むことを特徴とする紫外線硬化型組成物を提供する。

(A) 波長領域370nmから450nmにおいて、モル吸光係数が50 (l/mol*cm)以上となる点を有する光重合開始剤。

(B) 分子内開裂型または水素引き抜き型で(A)に属

used influences largely, is provided as information recording layer there are times when whitish degradation it does transparent heat resistant thermoplastic resin substrate.

[0005] In regard to this kind of substrate or other property change, it was known already, well that influence of ultraviolet light curable composition which is used is large was thought thing whose influence of reactive monomer and oligomer which generally, are used is large.

[0006] But, as for substrate or other degradation, because of that it is not something which the result is done, even when reactant which is expected that relatively the substrate and information recording layer or other degradation are little, selecting, with kinds of the photoinitiator which is included in ultraviolet light-curing composition, it is understood even from knowledge of these inventors that it receives big influence.

[0007]

[Problems to be Solved by the Invention] As for this invention considering to status which catches, it is something which you can do, it is to offer ultraviolet light-curable composition which gives the cured product which does not cause property change of substrate and information recording layer in under harsh environment.

[0008]

[Means to Solve the Problems] As for these inventors, In order to solve above-mentioned problem result of diligent investigation, reactive monomer and oligomer component were made same, property change extent of substrate and the information recording layer differed largely even in when only photoinitiator component was changed in under harsh environment, when ultraviolet light-curable composition is used as adhesive for the DVD, curability furthermore selection of photoinitiator discovering the fact that quite it is important reached to this invention even from the viewpoint of substrate property change.

[0009] Namely this invention each 1 kind or more which is selected from below-mentioned photoinitiator group (A) and (B) as adhesive which is used occasion where the 2 disk which at least possesses information recording layer in disk of one layer is pasted together, offers ultraviolet light-curable composition which designates that it includes as feature.

(A) From wavelength region 370 nm in 450 nm, photoinitiator which possesses point where the molar absorptivity becomes 50 (l/mol*cm) or greater.

(B) Photoinitiator which does not belong to (A) with intramole

さない光重合開始剤。

【0010】本発明に使用する光重合開始剤のうち、(A)に属する光重合開始剤としては、例えばベンゾインイソブチルエーテル、2,4-ジエチルチオキサントン、2-イソプロピルチオキサントン、2-クロロチオキサントン、ベンジル、2,4,6-トリメチルベンゾイルジフェニルホスフィンオキシド、2-ベンジル-2-ジメチルアミノ-1-(4-モルフォリノフェニル)-ブタノン-1、ビス(2,6-ジメトキシベンゾイル)-2,4,4-トリメチルペンチルホスフィンオキシド等が挙げられる。これら(A)群は、極めて減衰した弱い紫外線にも鋭敏に反応するものである。

【0011】これら光重合開始剤のうち、2,4,6-トリメチルベンゾイルジフェニルホスフィンオキシド、2-ベンジル-2-ジメチルアミノ-1-(4-モルフォリノフェニル)-ブタノン-1、ビス(2,6-ジメトキシベンゾイル)-2,4,4-トリメチルペンチルホスフィンオキシド等は基板を透過する紫外線に鋭敏に反応するため硬化性が優れている反面、酸素阻害を受けやすいため単独で用いる場合には、空気に触れる部分では硬化が不十分になる傾向がある。

【0012】光重合開始剤としては、波長領域370nmから450nmにおいて、モル吸光係数が50(l/mol*cm)以上、特に好ましくは、500(l/mol*cm)以上である点を有するものが良い。

【0013】(B)に属する光重合開始剤はこの欠点を解消するために併用できるものであり、分子内開裂型としてベンゾイルエチルエーテル、ベンジルジメチルケタール、1-ヒドロキシシクロヘキシルフェニルケトン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-オン、1-(4-イソプロピルフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン及び2-メチル-1-(4-メチルチオフェニル)-2-モルホリノプロパン-1-オン等を挙げることができる。

【0014】更に水素引き抜き型としては例えば、4-フェニルベンゾフェノン、イソフタロフェノン、4-ベンゾイル-4'-メチルジフェニルスルフィド等を挙げることができる。これら(B)群は、酸素による重合阻害を受け難いものである。

【0015】光重合開始剤群(A)及び(B)の併用割合は、特に制限されるものではないが、通常、(A)群/(B)群(重量比)=20/80~80/20、好ましくは60/40~40/60である。

【0016】また上記光重合開始剤に対し、増感剤として例えば、トリエチルアミン、メチルジエタノールアミン、トリエタノールアミン、ジエチルアミノアセトフェノン、p-ジメチルアミノアセトフェノン、p-ジメチ

cular cleavage type or the hydrogen-abstracting type.

[0010] You can list for example benzoin isobutyl ether, 2,4-diethyl thioxanthone, 2-isopropyl thioxanthone, 2-chloro thioxanthone, benzyl, the 2,4,6-trimethyl benzoyl diphenylphosphine oxide, 2-benzyl-2-di methylamino-1-(4-morpholino phenyl)-butanone-1 and bis(2,6-dimethoxy benzoyl)-2,4,4-trimethyl pentyl phosphine oxide etc among the photoinitiator which are used for this invention, as photoinitiator which belongs to the(A). It is something which reacts to also weak ultraviolet light where quite attenuation it did these (A) groups, acutely.

[0011] In order among these photoinitiator, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, 2-benzyl-2-di methylamino-1-(4-morpholino phenyl)-butanone-1 and the bis(2,6-dimethoxy benzoyl)-2,4,4-trimethyl pentyl phosphine oxide etc to react to ultraviolet light which transmits substrate acutely, while curability is superior, when to receive oxygen inhibition damages easily and uses with alone, with portion which is touched to air there is a tendency where hardening becomes insufficient.

[0012] As photoinitiator, those which possess point where molar absorptivity is the 50(l/mol*cm) or greater, particularly preferably and 500(l/mol*cm) or greater from wavelength region 370 nm in 450 nm, are good.

[0013] Photoinitiator which belongs to (B) is something which can be jointly used in order to cancel this deficiency, benzoyl ethyl ether, benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone and 2-hydroxy-2-methyl-1-phenyl-propane-1-on, 1-(4-isopropyl phenyl)-2-hydroxy-2-methyl propane-1-on and the 2-methyl-1-(4-methylthio phenyl)-2-morpholino-propanone-1-on etc can be listed as intramolecular cleavage type.

[0014] Furthermore for example 4-phenyl benzophenone, isophthalophenone and 4-benzoyl-4'-methyl-biphenyl sulfide etc can be listed as hydrogen-abstracting type. These (B) groups are something which is difficult to receive polymerization inhibition due to oxygen.

[0015] Combined proportion of photoinitiator group (A) and (B) is not something which is especially restricted. usually, (A) group / (B) group (weight ratio) = 20/80 to 80/20, it is a preferably 60/40 to 40/60.

[0016] In addition it is possible also to jointly use for example triethylamine, methyl diethanolamine, the triethanolamine, diethyl amino acetophenone, p-di methylamino acetophenone, ethyl p-dimethylaminobenzoate, isoamyl p-

ルアミノ安息香酸エチル、*p*-ジメチルアミノ安息香酸イソアミル、*N,N*-ジメチルベンジルアミン及び4、4'-ビス(ジエチルアミノ)ベンゾフェノン等の、後述重合性成分と付加重合反応を起こさないアミン類を併用することもできる。勿論、上記光重合開始剤や増感剤は、硬化性成分への溶解性に優れ、紫外線透過性を阻害しないものを選択して用いることが好ましい。

【0017】紫外線硬化性組成物を調製するに際しては、単官能(メタ)アクリレートや多官能(メタ)アクリレートを重合性モノマー成分として用いることができる。これらは各々、単独又は2種以上併用して使用することができる。しかしながら、2以上の(メタ)アクリロイル基を有する多官能(メタ)アクリレートの2種以上を必須成分として組成物を調製するのが良い。

【0018】本発明に使用できる重合性モノマーとしては例えば以下のものが挙げられる。単官能(メタ)アクリレートとしては例えば、置換基としてメチル、エチル、プロピル、ブチル、アミル、2-エチルヘキシル、オクチル、ノニル、ドデシル、ヘキサデシル、オクタデシル、シクロヘキシル、ベンジル、メトキシエチル、ブトキシエチル、フェノキシエチル、ノニルフェノキシエチル、テトラヒドロフルフリル、グリシジル、2-ヒドロキシエチル、2-ヒドロキシプロピル、3-クロロ-2-ヒドロキシプロピル、ジメチルアミノエチル、ジエチルアミノエチル、ノニルフェノキシエチルテトラヒドロフルフリル、カプロラクトン変性テトラヒドロフルフリル、イソボルニル、ジシクロペンタニル、ジシクロペンテニル、ジシクロペンテニロキシエチル等の如き基を有する(メタ)アクリレート等が挙げられる。

【0019】又、多官能(メタ)アクリレートとしては例えば、1,3-ブチレングリコール、1,4-ブタンジオール、1,5-ペンタンジオール、3-メチル-1,5-ペンタンジオール、1,6-ヘキサジオール、ネオペンチルグリコール、1,8-オクタンジオール、1,9-ノナンジオール、トリシクロデカンジメタノール、エチレングリコール、ポリエチレングリコール、プロピレングリコール、トリプロピレングリコール、ポリプロピレングリコール等のジアクリレート、トリス(2-ヒドロキシエチル)イソシアヌレート、ジ(メタ)アクリレート、ネオペンチルグリコール1モルに4モル以上のエチレンオキサイド若しくはプロピレンオキサイドを付加して得たジオールのジ(メタ)アクリレート、ビスフェノールA 1モルに2モルのエチレンオキサイド若しくはプロピレンオキサイドを付加して得たジオールのジ(メタ)アクリレート、トリメチロールプロパン1モルに3モル以上のエチレンオキサイド若しくはプロピレンオキサイドを付加して得たトリオールのジ又はトリ(

dimethylaminobenzoate, *N,N*-diethylbenzylamine and 4,4'-bis(diethylamino)benzophenone or other, later mentioned polymerizable component and the amines which does not cause addition polymerization reaction vis-a-vis above-mentioned photoinitiator, as sensitizer. Of course, above-mentioned photoinitiator and sensitizer are superior in the solubility to hardenable component, selecting those which do not obstruct ultraviolet light transmittance, it is desirable to use.

[0017] When ultraviolet light-curing composition is manufactured, it is possible to use monofunctional (meth)acrylate and the polyfunctional (meth)acrylate as polymerizable monomer component. Each, alone, 2 kinds or more jointly using, you can use these. But, it is good to manufacture composition with 2 kinds or more of polyfunctional (meth)acrylate which possesses (meth)acryloyl group of 2 or more as essential component.

[0018] You can list those below for example as polymerizable monomer which can be used for this invention. As monofunctional (meth)acrylate methyl, ethyl, propyl, butyl, amyl, the 2-ethylhexyl, octyl, nonyl, dodecyl, hexadecyl, octadecyl, the cyclohexyl, benzyl, methoxyethyl, butoxyethyl, phenoxyethyl, nonyl phenoxyethyl, the tetrahydrofurfuryl, glycidyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-chloro-2-hydroxypropyl, you can list dimethylaminoethyl, diethylaminoethyl, nonyl phenoxyethyl tetrahydrofurfuryl, caprolactam-modified tetrahydrofurfuryl and (meth)acrylate etc which possesses basis a isobornyl, dicyclopentanyll, dicyclopentenyl, dicyclopentenyl oxyethyl or other way as for example substituent.

[0019] As also, polyfunctional (meth)acrylate for example 1,3-butenylene glycol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,8-octanediol, 1,9-nonanediol, tricyclodecane dimethanol, ethyleneglycol, polyethylene glycol, propylene glycol, tripropylene glycol, polypropylene glycol or other diacrylate, Adding ethylene oxide or propylene oxide of 4 mole or more to di(meth)acrylate, neopentyl glycol 1 mole of tris(2-hydroxyethyl)isocyanurate, it acquires di(meth)acrylate of diol which, Adding ethylene oxide or propylene oxide of 2 mole to bisphenol A 1 mole, it acquires the di(meth)acrylate of diol which, Adding ethylene oxide or propylene oxide of 3 mole or more to trimethylolpropane 1 mole, di or tri(meth)acrylate of the triol which it acquires, adding ethylene oxide or propylene oxide of the 4 mole or more to bisphenol A 1 mole, di(meth)acrylate / tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate of diol which it acquires, the poly(meth)acrylate of poly(meth)acrylate / caprolactam-modified

メタ) アクリレート、ビスフェノール A 1 モルに 4 モル以上のエチレンオキサイド若しくはプロピレンオキサイドを付加して得たジオールのジ (メタ) アクリレート／トリス (2-ヒドロキシエチル) イソシアヌレートトリ (メタ) アクリレート、トリメチロールプロパントリ (メタ) アクリレート、ペンタエリスリトールトリ (メタ) アクリレート／ジペンタエリスリトールのポリ (メタ) アクリレート／カプロラクトン変性トリス [(メタ) アクリロキシエチル] イソシアヌレート、アルキル変性ジペンタエリスリトールのポリ (メタ) アクリレート、カプロラクトン変性ジペンタエリスリトールのポリ (メタ) アクリレート／ヒドロキシピバリン酸ネオペンチルグリコールジアクリレート、カプロラクトン変性ヒドロキシピバリン酸ネオペンチルグリコールジアクリレート／エチレンオキサイド変性リン酸 (メタ) アクリレート、エチレンオキサイド変性アルキル化リン酸 (メタ) アクリレート等があげられる。

【0020】また、N-ビニル-2-ピロリドン、アクリロイルモルホリン、ビニルイミダゾール、N-ビニルカプロラクタム、酢酸ビニル、(メタ) アクリル酸、(メタ) アクリルアミド、N-ヒドロキシメチルアクリルアミド又はN-ヒドロキシエチルアクリルアミド及びこれらのアルキルエーテル化合物等も使用できる。

【0021】更に、重合性モノマーと同様に併用できるものとしては、重合性オリゴマーとしてポリエステルアクリレート、ポリエーテルアクリレート、エポキシアクリレート、ウレタンアクリレート等がある。

【0022】金属薄膜を主体とする情報記録層へのより高い密着性を得るに当たっては、リン酸又はその誘導体からなる官能基を有する (メタ) アクリレート化合物を組成物中に含める様にし、硬度をより高めるためには、より多数の (メタ) アクリロイル基を 1 分子中に有する (メタ) アクリレート化合物を含める様に、同様に同一官能基数ではより多く含める様にし、弾性率等の調節には、重合性オリゴマーの様な比較的高分子の重合成分を含めたりする様にすることが出来る。

【0023】紫外線硬化型組成物としては、常温～40℃において、液状であるものを用いるのが好ましい。溶媒は用いないのが好ましく、用いたとしても極力少量に止めるのが好ましい。また、前記組成物の塗布をスピナーで行う場合には、粘度を 20～1000 センチポイズとなる様に調製するのが好ましく、比較的厚膜とする場合は 100～1000 センチポイズとなるように調製するのがよい。

【0024】本発明においては、当該記録層側同士を接着するが、露出した情報記録層同士を直接接着する様にしてもよいし、情報記録層の露出面を保護する保護コー

tris [(meth)acryloxy ethyl] isocyanurate, alkyl-modified dipentaerythritol of trimethylolpropane tri (meth)acrylate and pentaerythritol tri (meth)acrylate / dipentaerythritol, you can list poly (meth)acrylate / neopentyl glycol hydroxypivalate diacrylate, caprolactam-modified neopentyl glycol hydroxypivalate diacrylate / ethylene oxide modified phosphoric acid (meth)acrylate and ethylene oxide modified alkylation phosphoric acid (meth)acrylate etc of caprolactam-modified dipentaerythritol.

[0020] In addition, N - vinyl - 2 - pyrrolidone, you can use also acryloyl morpholine, the vinyl imidazole, N - vinyl caprolactam, vinyl acetate, (meth)acrylic acid, (meth)acrylamide, N - hydroxymethyl acrylamide or the N - hydroxyethyl acrylamide and those alkyl ether compound etc.

[0021] There is a polyester acrylate, polyether acrylate, epoxy acrylate and a urethane acrylate etc as polymerizable oligomer as can be jointly used in same way as polymerizable monomer, furthermore.

[0022] When adhesion where is higher to information recording layer which designates metal thin film as main component is obtained, It tries to include (meth) acrylate compound which possesses functional group which consists of phosphoric acid or its derivative in composition, in order to raise from hardness, from in order to include (meth) acrylate compound which possesses multiple (meth)acryloyl group in the 1 molecule, in same way with same number of functional groups more to include it tries, to modulus or other adjustment fact that it tries to include polymerizing ingredient of the comparative polymer like polymerizable oligomer it is possible.

[0023] As ultraviolet light-curable composition, it is desirable to use those which are a liquid in the ambient temperature to 40℃. solvent it is desirable not to use, assuming, that it used, it is desirable to stop in forcible trace. In addition, when it applies aforementioned composition with spin coater, it is desirable in order to become 20 to 1000 centipoise, to manufacture the viscosity, when it makes thick film relatively, in order to become the 100 to 1000 centipoise, it is good to manufacture.

[0024] Regarding to this invention, it glues this said recording layer side, but it is possible to glue the information recording layer which is exposed directly and, providing protective

ト層をその上に設けて、その保護コート層同士を接着する様にしてもよい。この場合、この保護コート層も、通常、紫外線硬化型組成物の硬化物で形成される。その場合にこの保護コート層は、紫外線透過性とする必要がある。保護コート層用の紫外線硬化型組成物は、情報記録層の露出面と、ディスク同士を接着するための紫外線硬化型組成物の硬化物との両方に接着性に優れる様に調製するのが好ましい。

【0025】また、本発明の組成物には、必要であれば、さらにその他の添加剤として、熱重合禁止剤、ヒンダードフェノール、ヒンダードアミン、ホスファイト等に代表される酸化防止剤、可塑剤及びエポキシシラン、メルカプトシラン、(メタ)アクリルシラン等に代表されるシランカップリング剤等を、各種特性を改良する目的で、従来の使用量で配合することもできる。これらは、硬化性成分への溶解性に優れたもの、紫外線透過性を阻害しないものを選択して用いる。

【0026】本発明の組成物を調製するに当たっては、上記光重合開始剤のみならず、組成物そのものの物性及び貼り合わせ硬化層の物性をDVDに適したものとなる様に化学組成を適宜選択する。

【0027】この際の基準としては、情報記録層に記録された情報の変質、即ちピットに異常が生じないことが大前提として、例えば、塗布温度条件下で、組成物中の成分が結晶化したり相分離することがないこと、貼り合わせる2つの表面いずれに対しても極力高い濡れ性を有していること、短時間に平滑で均一な湿潤表面を与えるレベリング性を有していること、貼り合わせる2つ表面を腐蝕や劣化させる原因物質やイオンを極力含まないこと、硬化前の組成物に液状においてもある程度の粘着性を有していること、硬化阻害の一因となる気体の溶解度が極力小さいこと、組成物が硬化前でも硬化後でも紫外線を出来るだけ高率で透過する透明性があること、硬化後の接着層と基板を構成する耐熱性熱可塑性樹脂との間の屈折率や硬度が極力同じであること、貼り合わせた2層と硬化層の密着性がより大きくなる様にすること、同硬化層の弾性率を特定範囲とする様にすること、同硬化層の透湿度を極力小さくする様にすること、同組成物の硬化前と硬化後の収縮率を極力小さくする様にすること、そしてこれらの各評価項目での測定値が、絶対値として優れており、かつ常態時と、高温高湿長時間被曝時とでそれら各絶対値間の変化が極力小さいこと等が挙げられる。これら基準を全て満足するか、出来るだけ多く満足する様に、光重合開始剤を含む紫外線硬化型組成物

coating which protects exposed surface of information recording layer on that, it is possible to glue the protective coating. In this case, also this protective coating, is usually formed with the cured product of ultraviolet light-curable composition. As for this protective coating, it is necessary in that case to make ultraviolet light transmittance. As for ultraviolet light-curable composition for protective coating, in order exposed surface of information recording layer and the cured product of ultraviolet light-curable composition in order to glue disk in both to be superior in adhesiveness, it is desirable to manufacture.

[0025] In addition, if, it is necessary in composition of this invention, with the objective which improves various properties, also to combine with conventional amount used it is possible antioxidant which is represented in thermal polymerization inhibitor, hindered phenol, the hindered amine and phosphite etc furthermore as other additive, and silane coupling agent etc which is represented in plasticizer and epoxy silane, mercapto silane and the (meth)acrylic silane etc. As for these, those which are superior in solubility to hardenable component. Selecting those which do not obstruct ultraviolet light transmittance, it uses.

[0026] When composition of this invention is manufactured, in order the above-mentioned photoinitiator furthermore, property of composition itself and the property of laminated hardened layer to become something which is suited for the DVD, chemical composition is selected appropriately.

[0027] In this case as reference, Is recorded to information recording layer degradation of information which, Namely fault not occurring in pit major premise doing, With under for example application temperature condition, component in composition does and/or crystallization times when phase separation it does is, Possessing forcible high wettability vis-a-vis 2 surface which which it paste together it is, Possessing leveling behavior which gives uniform wetting surface to short time with smooth it is, two surface which it pastes together causing substance and ion which it corrodes and deteriorate and forcible it includes, Possessing viscous adhesiveness of certain extent in composition before hardening regarding liquid state, it is, solubility of gas which becomes cause of hardening inhibition forcible is small thing, Even when composition before hardening, even after hardening transparency which transmits ultraviolet light as much as possible with high rate it is, index of refraction and hardness with adhesive layer after hardening and heat resistant thermoplastic resin which forms substrate being forcible same, it is, That adhesion of 2 layers and cured layer which it pastes together becomes larger it does, To designate modulus of same cured layer as certain range it does, It tries moisture permeability of same cured layer to make forcible small, it tries the shrinkage ratio before hardening same

は調製される。

【0028】更に本発明の組成物は、硬化のための紫外線照射方式として、一般的に広く行われている連続光照射を用いる以外にも、従来の連続光照射で硬化に必要な照射光量と同量又はより少ない光量を、例えば $\mu\text{sec} \sim \text{msec}$ オーダの短時間に一気に照射する、閃光照射方式で行ってもよい。

【0029】光照射は、対向させたディスクの片側面のみから行ってもよいが、両面から行うようにすることも出来る。

【0030】本発明の組成物は、デジタルビデオディスクの製造方法において、例えば、耐熱性熱可塑性樹脂に情報記録薄膜が積層されたディスク基板1枚と、耐熱性熱可塑性樹脂のみからなる基板との接着に、特に有効である。厳しい環境条件下における基板の白濁や白化の防止効果は、それを構成する耐熱性熱可塑性樹脂がポリカーボネートである場合に顕著である。

【0031】この場合には、各基板を対向させてから、通常、耐熱性熱可塑性樹脂のみからなる基板側から、紫外線を照射して本発明の組成物を硬化して接着する。

【0032】

【発明の実施の形態】次に本発明の実施形態を好ましい態様に基づいて説明する。まず400～600オングストロームの金属薄膜が積層された円盤状プラスチック基板を1枚と、円盤状プラスチックのみからなる基板1枚を準備する。

【0033】次いで、2以上の(メタ)アクリロイル基を有する多官能(メタ)アクリレート2種以上を必須成分かつ主成分とし、必要に応じて重合性モノマーをも用いて、光重合開始剤(A)として370nm以上の領域に吸収波長を有し、かつ波長領域370nmから450nmにおいて、モル吸光係数が50 (l/mol cm) 以上である点を有するものと、同(B)として、分子内開裂型または水素引き抜き型で(A)に属さない光重合開始剤

composition and after hardening to make the forcible small, and measured value in these each evaluation criteria, is superior as the absolute value, at same time at time of ordinary state and at time of the high temperature high humidity lengthy exposure forcible small thing etc can list change between those each absolute value. These reference all are satisfied, or in order to be satisfied as mainly as possible, ultraviolet light-curable composition which includes photoinitiator is manufactured.

[0028] Furthermore in addition to composition of this invention a continuous illumination which is widely done generally as ultraviolet irradiation system for hardening, using, a less light intensity, to short time of for example sec to msec order at a stroke irradiation dose and same amount which are necessary for hardening with conventional continuous illumination or irradiates, with the flash illumination system to do it is possible.

[0029] May do illumination, from only one side surface of disc which opposes, but it is possible also to try to do from both surfaces.

[0030] Composition of this invention, in glueing with disk substrate one layer where information recording thin film is laminated to for example heat resistant thermoplastic resin in manufacturing method of digital video disk, and substrate which consists of only heat resistant thermoplastic resin, especially is effective. clouding of substrate in under harsh environmental condition and preventing effect of the whitening are remarkable when heat resistant thermoplastic resin which forms that is polycarbonate.

[0031] In this case, after each substrate opposing, usually, from the substrate side which consists of only heat resistant thermoplastic resin, irradiating ultraviolet light, hardening composition of this invention, it glues.

[0032]

[Embodiment of Invention] Next embodiment of this invention is explained on basis of desirable embodiment. First disc shape plastic substrate where metal thin film of 400 to 600 Angstrom is laminated substrate one layer which consists of only one layer and disc shape plastic is prepared.

[0033] Next, polyfunctional (meth)acrylate 2 kinds or more which possesses (meth) acryloyl group of 2 or more essential ingredient and the main component to do, Using also according to need polymerizable monomer, it possesses absorption wavelength in region of 370 nm or greater as photoinitiator (A), ultraviolet light-curable composition per 100 parts by weight meter 2 to 7 parts by weight of liquid state using photoinitiator which does not belong to (A) with intramolecular cleavage type

を、液状の紫外線硬化型組成物 100 重量部当たり計 2 ~ 7 重量部使用して、組成物を調製する。但し、ベンゾフェノン、この組成物中には含めない様にする。

【0034】より好適な光重合開始剤群 (A) 及び (B) の選択的組み合わせは、次の通りである。

光重合開始剤群 (A) : 波長領域 370 nm から 450 nm において、モル吸光係数が 500 (l/mol*cm) 以上となる点を有するもの。

光重合開始剤群 (B) : ベンゾイルエチルエーテル、ベンジルジメチルケタル、1-ヒドロキシシクロヘキシルフェニルケトン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-オン、1-(4-イソプロピルフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン、2-メチル-1-(4-メチルチオフェニル)-2-モルホリノプロパン-1-オン (以上、分子内開裂型光重合開始剤)、4-フェニルベンゾフェノン、イソフタルフェノン、4-ベンゾイル-4'-メチルジフェニルスルフィド (以上、水素引き抜き型光重合開始剤)。

【0035】前記組成物を前記基板の金属薄膜面に塗布し、お互いの基板面同志を貼り合わせてから、両プラスチック基板面から紫外線を照射して、両者を接着させ DVD とする。

【0036】

【実施例】次に実施例を挙げて本発明を詳細に説明するが、本発明はこれらの実施例に限定されるものではない。尚、以下実施例中「部」は「重量部」を表す。

【0037】実施例 1

ネオペンチルグリコールジアクリレート 20 部、ビスフェノール A 1 モルにエチレンオキサイド 2 モル反応させたジオールのジアクリレート 20 部、トリメチロールプロパントリアクリレート 30 部、ポリテトラメチレングリコール (分子量 850) 1 モルとトリレンジイソシアネート 2 モル反応後ヒドロキシエチルアクリレート 2 モルを反応させて得たウレタンアクリレート 26 部、光重合開始剤として 2, 4, 6-トリメチルベンゾイルジフェニルホスフィンオキシド 2 部及びベンジルジメチルケタル 2 部を 60 °C で 1 時間混合溶解し、淡黄色透明の紫外線硬化型組成物を作製した。この組成物を用いて下記試験方法 1 により貼り合わせディスクを作製し、ディスク端面を指触したところタック性はなかった。またこ

or hydrogen-abstracting type those which possess point where molar absorptivity is 50 (l/mol*cm) or greater at same time in the 450 nm, same (B) as from wavelength region 370 nm,, it manufactures composition. However, it tries benzophenone, not to include in this composition.

[0034] From selective combination of preferred photoinitiator group (A) and (B) is as follows.

From photoinitiator group (A): wavelength region 370 nm in 450 nm, those which possess the point where molar absorptivity becomes 500 (l/mol*cm) or greater.

Photoinitiator group (B): benzoyl ethyl ether, benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone and 2-hydroxy-2-methyl-1-phenyl-propane-1-on, 1-(4-isopropyl phenyl)-2-hydroxy-2-methyl propane-1-on, 2-methyl-1-(4-methylthio phenyl)-2-morpholino-propanone-1-on (Above, intramolecular cleavage type photoinitiator), 4-phenyl benzophenone, isophthalophenone and 4-benzoyl-4'-methyl-biphenyl sulfide (Above, hydrogen abstracting photopolymerization initiator).

[0035] To apply aforementioned composition to metallic thin film surface of aforementioned substrate, after pasting together mutual substrate surface, irradiating ultraviolet light from both plastic substrate surface, glueing both, it makes DVD.

[0036]

[Working Example(s)] Listing Working Example next, you explain this invention in detail, but this invention is not something which is limited in these Working Example. Furthermore, "part" in Working Example below displays "parts by weight"

[0037] Working Example 1

1 hour it mixed melted 2,4,6-trimethyl benzoyl diphenyl phosphine oxide 2 part and benzyl dimethyl ketal 2 part with 60 °C ethylene oxide 2 mole the diacrylate 20 part of diol which reacts, as urethane acrylate 26 part and photoinitiator which after trimethylolpropane triacrylate 30 part, polytetramethylene glycol (molecular weight 850) 1 mole and toluene diisocyanate 2 mole reaction reacting, acquire hydroxyethyl acrylate 2 mole in the neopentyl glycol diacrylate 20 part, and bisphenol A 1 mole produced ultraviolet light-curable composition of pale yellow transparent. Making use of this composition when it produces laminated disk with the below mentioned test method 1, finger contact it does disk endface there was not attackiness. In addition this disk external

のディスクを85℃95%RH環境下96時間経過後外観観察したところ、環境試験前と比較し全く変化がなかった。

【0038】〈試験方法1〉金属薄膜としてアルミニウムを500オングストロームの膜厚に形成した直径12cmの円盤状ポリカーボネート基板を2枚作製し、その1枚に、上記組成物をディスペンサで塗布し、ついでもう一枚の基板を重ね合わせた。塗布量は基板の自重のみで上記組成物を押し上げた時に当該組成物の膜厚が20～50μmになるようにした。ついで、照射強度55mW/cm²に調整した集光型メタルハライドランプ（コールドミラー付き、ランプ出力80W/cm）を設置したベルトコンベア式紫外線照射装置を用い、コンベアスピード3m/min（照射光量約230mJ/cm²）で硬化した。尚、2つのポリカーボネート基板面両方からの光照射を行った。

【0039】実施例2

重合性成分は上記実施例1と同一とし、光重合開始剤として2-ベンジル-2-ジメチルアミノ-1-（4-モルフォリノフェニル）-ブタノン-1を2部及びベンジルジメチルケタール2部を60℃で1時間混合溶解し、淡黄色透明の紫外線硬化型組成物を作製した。この組成物を用い実施例1と同様に貼り合わせディスクを作製し、ディスク端面を指触したところタック性はなかった。85℃95%RH環境下96時間経過後外観観察したところ、環境試験前と比較し全く変化がなかった。

【0040】実施例3

重合性成分は上記実施例1と同一とし、光重合開始剤として2, 4, 6-トリメチルベンゾイルジフェニルホスフィンオキシド2部及びベンジルジメチルケタール2部を60℃で1時間混合溶解し、淡黄色透明の紫外線硬化型組成物を作製した。この組成物を用いて下記試験方法2により貼り合わせディスクを作製し、ディスク端面を指触したところタック性はなかった。またこのディスクを85℃95%RH環境下96時間経過後外観観察したところ、環境試験前と比較し全く変化がなかった。

〈試験方法2〉金属薄膜としてアルミニウムを500オングストロームの膜厚に形成した直径12cmの円盤状ポリカーボネート基板に、上記組成物をディスペンサで塗布し、ついで直径12cmの透明円盤状ポリカーボネート基板を重ね合わせた。塗布量は基板の自重のみで上

appearance observation after 96-hour lapse under 85 °C 95 %RH environment when it does, completely there was not change by comparison with before the environmental test.

[0038] [Test method 1] Disc shape polycarbonate substrate of diameter 12 cm which formed aluminum in film thickness of the 500 Angstrom as metal thin film 2 was produced, above-mentioned composition was applied to one layer, with dispenser, substrate of one layer was already superposed next. coating amount pushed above-mentioned composition with only its own weight of the substrate and when expanding, film thickness of this said composition tried that become the 20 to 50 μm. Next, it hardened with conveyor speed 3 m/min (irradiation dose approximately 230 mJ/cm²) making use of belt conveyor type ultraviolet light illumination equipment which installs focusing metal halide lamp (cold mirror-equipped and lamp output 80 W/cm) which was adjusted illumination intensity 55 mW/cm². Furthermore illumination from 2 polycarbonate substrate surface both was done.

[0039] Working Example 2

Polymerizable component made same as above-mentioned Working Example 1, with 60 °C 1 hour mixed melted 2 - benzyl - 2-di methylamino - 1 - (4 - morpholino phenyl) - butanone - 1 2 part and benzyl dimethyl ketal 2 parts photoinitiator, produced ultraviolet light-curable composition of pale yellow transparent. When it produces laminated disk in same way as Working Example 1 making use of this composition, finger contact it does disk endface there was not a tackiness. external appearance observation after 96-hour lapse under 85 °C 95 %RH environment when it does, completely there was not change by comparison with before environmental test.

[0040] Working Example 3

Polymerizable component made same as above-mentioned Working Example 1, with 60 °C 1 hour mixed melted 2,4,6 - trimethyl benzoyl diphenylphosphine oxide 2 part and benzyl dimethyl ketal 2 part as photoinitiator, produced the ultraviolet light-curable composition of pale yellow transparent. Making use of this composition when it produces laminated disk with the below-mentioned test method 2, finger contact it does disk endface there was not a tackiness. In addition this disk external appearance observation after 96-hour lapse under 85 °C 95 %RH environment when it does, completely there was not change by comparison with before the environmental test.

[Test method 2] Above-mentioned composition was applied to disc shape polycarbonate substrate of diameter 12 cm which formed aluminum in film thickness of 500 Angstrom as metal thin film, with the dispenser, transparent disc shape polycarbonate substrate of diameter 12 cm was superposed next

記組成物を押し拡げた時に当該組成物の膜厚が20～50 μmになるようにした。ついで、照射強度55 mW/cm²に調整した集光型メタルハライドランプ（コールドミラー付き、ランプ出力80 W/cm）を設置したベルトコンベア式紫外線照射装置を用い、コンベアスピード3 m/min（照射光量約230 mJ/cm²）で硬化した。尚、ポリカーボネートのみからなる基板とアルミニウム薄膜が積層された両ポリカーボネート基板面からの光照射を行った。

【0041】実施例4

重合性成分は上記実施例1と同一とし、光重合開始剤として2-ベンジル-2-ジメチルアミノ-1-(4-モルフォリノフェニル)-ブタノン-1を2部及びベンジルジメチルケタール2部を60℃で1時間混合溶解し、淡黄色透明の紫外線硬化型組成物を作製した。この組成物を用い実施例3と同様に貼り合わせディスクを作製し、ディスク端面を指触したところタック性はなかった。85℃95%RH環境下96時間経過後外観観察したところ、環境試験前と比較し全く変化がなかった。

【0042】実施例1～4の(A)群の光重合開始剤は、いずれも、370 nm以上の領域に吸収波長を有し、370から450 nmにおいて、モル吸光係数が500 (l/mol*cm) 以上となる点を有していた。

【0043】また、実施例1～4の組成物で貼り合わせた、金属薄膜層が積層された耐熱性熱可塑性樹脂基板の金属薄膜層同志を貼り合わせたDVD、金属薄膜層が積層された耐熱性熱可塑性樹脂基板の金属薄膜層と、耐熱性熱可塑性樹脂のみからなる基板とを貼り合わせたDVDは、いずれの場合においても、例えば高温高湿に長時間被曝されるという厳しい環境下においても、DVDに変質が見られないことがわかる。

【0044】しかも、実施例1～4の組成物は、上記した技術的他にも、次の2点の長所も兼備している。即ち、効率のよい硬化接着が出来るという硬化性の点でも、貼り合わせディスクの端面からはみ出た部分にもタック性が認められないという点でも優れているのである。

coating amount pushed above-mentioned composition with only its own weight of the substrate and when expanding, film thickness of this said composition tried that become the 20 to 50 μm. Next, it hardened with conveyor speed 3 m/min (irradiation dose approximately 230 mJ/cm²) making use of belt conveyor type ultraviolet light illumination equipment which installs focusing metal halide lamp (cold mirror-equipped and lamp output 80 W/cm) which was adjusted illumination intensity 55 mW/cm². Furthermore illumination from both polycarbonate substrate surface where substrate and the aluminum thin film which consist of only polycarbonate are laminated was done.

[0041] Working Example 4

Polymerizable component made same as above-mentioned Working Example 1, with 60 °C 1 hour mixed melted 2 - benzyl - 2-di methylamino - 1 - (4 - morpholino phenyl) - butanone - 1 2 part and benzyl dimethyl ketal 2 parts photoinitiator, produced ultraviolet light-curable composition of pale yellow transparent. When it produces laminated disk in same way as Working Example 3 making use of this composition, finger contact it does disk endface there was not a tackiness. external appearance observation after 96-hour lapse under 85 °C 95 %RH environment when it does, completely there was not change by comparison with before environmental test.

[0042] Photoinitiator of (A) group of Working Example 1 to 4, in each case, had absorption wavelength in the region of 370 nm or greater, had possessed point where molar absorptivity becomes 500 (l/mol*cm) or greater in 370 to 450 nm.

[0043] In addition, With composition of Working Example 1 to 4 it pastes together, As for DVD which pastes together with metal thin film layer of heat resistant thermoplastic resin substrate where DVD and metal thin film layer which paste together metal thin film layer of the heat resistant thermoplastic resin substrate where metal thin film layer is laminated are laminated and substrate which consists of only heat resistant thermoplastic resin, in under harsh environment that, in and the lengthy exposure it makes which in for example high temperature high humidity, what you cannot see property change in DVD understands.

[0044] Furthermore, composition of Working Example 1 to 4, has combined to other than technically which was inscribed, also strength of following 2 points. Namely, hardening adhesion whose efficiency is good is possible, it is superior in point that and you see from edge surface of laminated disk in point of curability that which appears and or you cannot recognize tackiness in portion.

【0045】実施例1～4の組成物は、いずれも貼り合わせ方式のDVD用接着剤として使用する紫外線硬化型組成物として好適であった。

【0046】尚、実施例では紫外線照射方式として一般的に広く行われている連続点灯光を用いたが、上記した様な閃光式照射方式で行っても良いのは勿論である。

【0047】

【発明の効果】本発明の組成物を使用することにより、高温高湿の環境試験という厳しい環境に被曝した後においても貼り合わせディスクの変質を起こさないで、耐久性に優れ信頼性の高いDVDを生産することが出来る。

[0045] Composition of Working Example 1 to 4 in each case was as ideal as adhesive for the DVD of laminated type as ultraviolet light-curable composition which you use.

[0046] Furthermore with Working Example continuous lamp light which is widely done generally as the ultraviolet irradiation system was used, but fact that it is good doing with the kind of flash type illumination which was inscribed is of course.

[0047]

[Effects of the Invention] Exposure after doing because degradation of laminated disk is not caused in, in harsh environment, environmental test of high temperature high humidity by using composition of the this invention, it is superior in durability and it is possible to produce the DVD where reliability is high.